Journal of Alloys and Compounds 509 (2011) 6296–6301

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effects of equal channel angular extrusion and aging treatment on R phase transformation behaviors and Ti_3Ni_4 precipitates of Ni-rich TiNi alloys

Xiaoning Zhang[a], Baoyu Xia[b,c], Jie Song[a], Bin Chen[d], Xiaolin Tian[d], Yingmin Hao[d], Chaoying Xie[a,*]

[a] State Key Lab. of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
[b] Energy Research Institute, Nanyang Technological University, 70 Nanyang Drive 637457, Singapore
[c] School of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive 637457, Singapore
[d] Materials Testing & Analysis Center, School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

ARTICLE INFO

Article history:
Received 17 December 2010
Received in revised form 4 March 2011
Accepted 8 March 2011
Available online 17 March 2011

Keywords:
TiNi
Equal channel angular extrusion (ECAE)
Aging
R-phase transformation
Ti_3Ni_4

ABSTRACT

Ni-rich TiNi alloys were subjected to the effect of multiple equal channel angular extrusion (ECAE) treatments by B_C path at 500 °C. The characteristics of R phase transformation in aging treatment were dissimilar in the appearance and the temperature range to those counterparts induced by ECAE treatments. The fine lens-like shape Ti_3Ni_4 particles precipitated mainly in the regions of near grain boundaries and on the tangled grain boundaries after ECAE treatments. The effects and mechanisms of aging treatments and ECAE treatments on R phase transformation behaviors and Ti_3Ni_4 precipitates were investigated and discussed.

1. Introduction

As one of the high strain processing ways, equal channel angular extrusion (ECAE) technique has been applied in the production of various ultrafine-grained materials [1–9]. The main ECAE advantage is that imposes a high plastic deformation during pressing without reducing the cross sectional area of working billets. Metals/alloys with the unique combinations of mechanical properties and ultrafine grains can be produced successfully by ECAE technique.

Recently, there were the extensive interests in the ECAE research, and many successful applications have been reported for various metal and alloy materials with ultrafine grains, such as TiNi alloys [10–17], TiAl and TiNb alloys [18,19],Ti [20–22], Mg and Cu alloys [23,24] etc. Among these ultrafine grain materials, Ni-rich TiNi alloys have many applications in engineering and medical fields for their superior properties, such as the shape memory effect (SME) and the pseudoelasticity (PE) [11,25]. The SME and PE properties, which related to martensite phase transformation, were extensively studied in scientific and technological fields [26]. It is well known that Ni-rich TiNi alloys exist three different phases, the B2 parent phase, the B19′ phase and the R phase [27,28]. Three phase transformations can happen possible, which correspond to B2 ↔ B19′ transformation, B2 ↔ R transformation and R ↔ B19′ transformation, respectively. Therefore, different combinations of these phase transformations can be observed under various technological processes [28].

R transformation can be introduced by different methods such as annealing after cold working [29], adding Al or Fe elements in TiNi alloys [30,31]. For Ni-rich TiNi alloys, both aging treatment [32,33] and ECAE treatments [13,14] could lead to the R phase transformation. To date, the mechanism of R phase transformation in Ni-rich TiNi alloys with the aging treatment and the following multiple ECAE treatments are seldom studied systematically. It is still inconclusive whether R transformation in ECAE treatments is induced by ECAE or the aging treatment on TiNi billets before ECAE. In this study, the R phase transformation behaviors of Ni-rich TiNi alloys after aging treatment and subsequent multiple ECAE treatments at warm 500 °C by B_C path are investigated. The reasons and differences of the special R phase transformation behaviors and Ti_3Ni_4 precipitates of positions and appearances with different ECAE treatments are also discussed. This investigation will be helpful for better understanding the R phase transformation behaviors of Ni-rich TiNi alloys after aging and ECAE treatments.

2. Experimental details

The initially hot forged Ni-rich Ti–50.9 at.% Ni alloy (nominal composition) rods with an initial average grain size of ~70 μm were annealed at 850 °C for 1 h (Fig. 3a), and then quenched into water quickly (solution treatment). The inner contact angle (Φ) and the arc of curvature (Ψ) at the outer point of contact between channels of

* Corresponding author. Tel.: +86 21 5474 2608.
E-mail addresses: zxn100@gmail.com (X. Zhang), cyxie@sjtu.edu.cn (C. Xie).

0925-8388/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.03.062

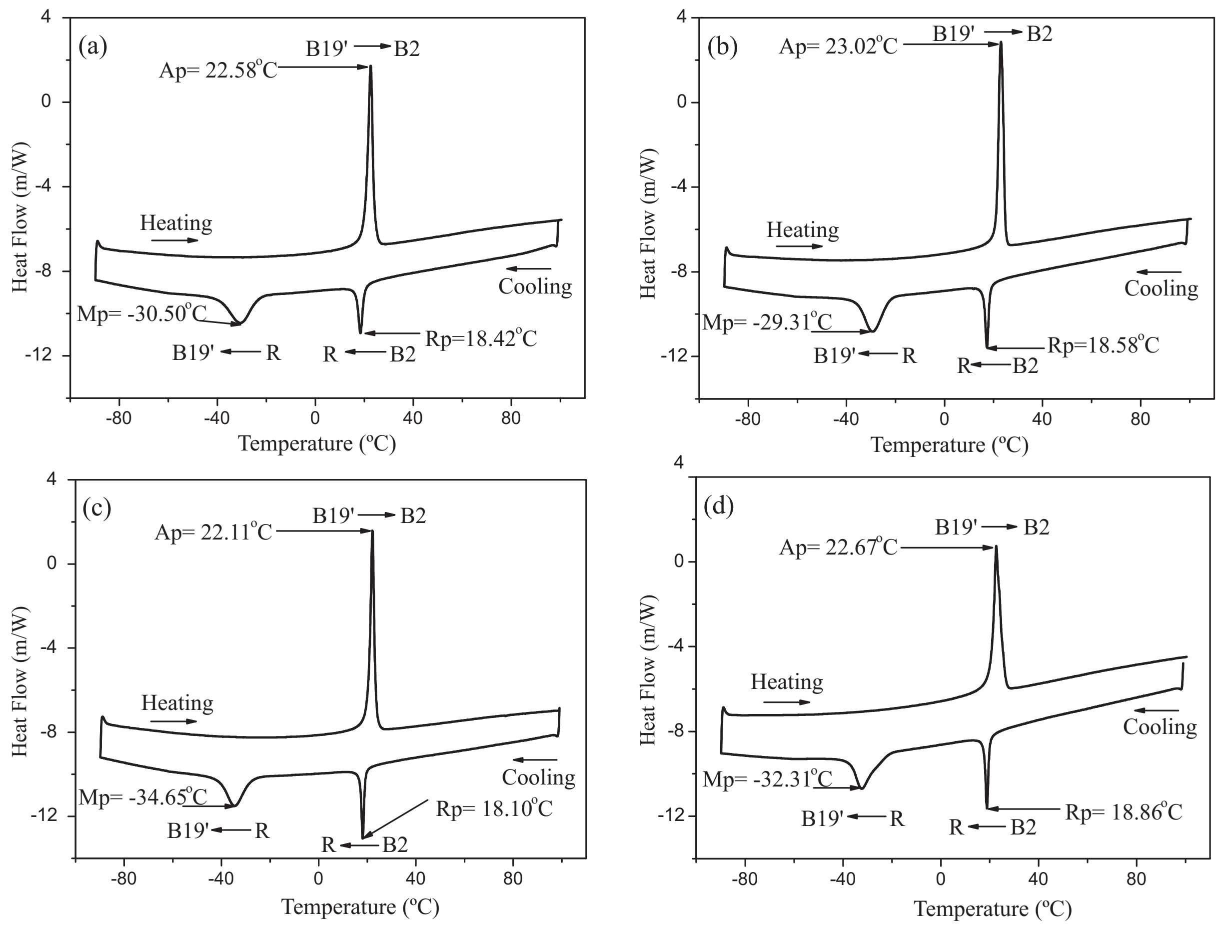

Fig. 1. DSC curves of Ti–50.9 at.% Ni alloy with the aging treatment at 500 °C for 20 min before ECAE treatments at 500 °C by B_C path: (a) first pass; (b) second pass; (c) fourth pass; (d) eighth pass.

the die were both 90°. It was well known that an effective strain of ~1 produced in the single pass of ECAE treatments. The hard-to-deformed Ti–50.9 at.% Ni alloy required a good plasticity to prevent cracking and fracture during ECAE treatments. For this reason, TiNi billets with dimensions of 10 mm × 10 mm × 140 mm need to be processed at 500 °C by B_C path (the billet was rotated by 90° either clockwise or anti-clockwise). And during every ECAE process, the billets were preheated at 500 °C for 20 min. The heated billets surfaces convenient solidified and coated with fluid graphitic lubricant. Graphitic lubricant can minimize the friction, prevent cracking and avoid the surface oxidation of working billets during the ECAE processes. Moreover, the ECAE processes cannot be considered as a thermo-mechanical treatment because the whole duration time of ECAE treatments is less than 10 s under the 8 mm/s constant velocity of ECAE processes.

For the differential scanning calorimeter (DSC) measurements, the metallographic examinations and transmission electron microscopy (TEM) observations, the samples were cut from the longitudinal plane of deformed billets that parallel to the extrusion direction of ECAE. The DSC measurements were carried out with heating and cooling rate 10 °C/min and samples weights of DSC test were between 5 and 10 mg. The range of DSC test temperatures was in −90 to 100 °C by using Diamond DSC machine (PerkinElmer Company of American). The metallographic experiments were performed with Zeiss optical microscope. Samples for TEM observation were prepared by twin jet electro-polishing at −30 °C and with manipulation voltage of 30 V. The twin jet solution was H_2SO_4 and CH_3OH mixture with a volume ratio of 1:4. TEM experiments were conducted on the JEM-2100F (JEOL) with an accelerating voltage of 200 kV.

3. Results

3.1. DSC analyses

R phase transformation behaviors of Ti–50.9 at.% Ni alloy with aging treatment at 500 °C for 20 min and different ECAE treatments were analyzed by DSC measurements, as shown in Figs. 1 and 2, respectively. The phase transformation temperatures of the martensite, R and austenite phase start (Ms, Rs, As), peak (Mp, Rp, Ap) and finish (Mf, Rf, Af) temperature of Ti–50.9 at.% Ni alloy with aging treatment and different ECAE passes were listed in Table 1.

When the specimen was cooled from 100 °C down to −90 °C, two exothermic peaks appeared obviously, which corresponded to from the B2 → R phase and then from the R → B19′ martensite phase transformation. The curves of B2 → R phase transformation of aging treatment were very sharp and clear, as shown in Fig. 1. It indicated that R phase transformation occurred in a very narrow temperature range. However, B2 → R phase transformation of ECAE treatments occurred in a wider temperature extent, and these broad and smooth curves were not very clear peaks (Fig. 2). Additionally, only R phase transformation was observed even the specimen was cooled till −150 °C after the first ECAE pass (Fig. 2a).

When the specimen was heated from −90 °C up to 100 °C, only one endothermic peak appeared. It showed that the reverse B19′ → R phase transformation and the subsequent reverse R → B2 martensite transformation overlapped together [34]. The very clear and apparent DSC curves of aging treatment also revealed the reverse transformation in a narrow temperature range (Fig. 1). However, the broad reverse transformation curves of ECAE treatments indicated that it occurred in a wider temperature range (Fig. 2). Moreover, the Mp, Rp and Ap of aging treatments were stable relatively (Table 1), and no obvious changes were happened after the different ECAE treatments (Fig. 1). However, the Mp and Ap after ECAE have a clear change along with the number of ECAE treatment increases, which are inconsistent with those of aging treatments.